THESIS

THE ADSORPTION OF GASEOUS HYDROCARBONS

on a

COCONUT CHARCOAL SERIES.

by

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FACULTY OF ARTS AND SCIENCES:

This is to certify that the undersigned have
read and recommended to the Committee on Graduate Studies
for acceptance, a thesis submitted by M.A. Nay, B.Sc.,
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Coconut Charcoal Series.

THE ADSORPTION OF GASEOUS HYDROCARBONS

on a

COCONUT CHARCOAL SERIES.

Submitted in Partial Fulfillment

of the Requirements for the

Degree of Master of Science.

by

M.A. NAY, B.Sc.

Under the direction of Dr. J.L. Morrison.

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HISTORICAL INTRODUCTION.

Historical Introduction

The phenomenon of adsorption was first discovered and described by C.W. Scheele in 1773. In the early history of its study the nature of adsorption was not known, hence was made synonymous with absorption. Subsequently it was recognized that the phenomenon occurred on the surface and the term adsorption was applied to this behavior. Adsorption now describes the behavior of a solid substance (adsorbent) in contact with a liquid or gas (adsorbate) which gives rise to an increase concentration of the adsorbate molecules on the surface of the adsorbent as compared with the bulk phase of the adsorbate.

Adsorption was found to be of two types depending on how the adsorbate molecule was held by the surface. In physical adsorption the molecules are held by Van der Waal's forces. In chemical adsorption the molecules are held by chemical bonds. The type encountered in this work is physical adsorption.

The phenomenon of adsorption is of great practical and theoretical importance in chemistry and allied sciences. The nature of adsorption has been the subject for a number of hypotheses, some of them contradicting each other. Possibly the most important of these is one brought forward by Langmuir in his classical paper on adsorption (1). In this paper he

states his mono-molecular layer theory which has been substantiated by much experimental evidence.

The mechanism of physical adsorption of adsorbates on various adsorbents has been investigated and determined. It has been found that the amount of material adsorbed is dependent on the concentration (or pressure in the case of gases) of the adsorbate, tempera-ture, time and the nature of the adsorbate and adsorbent. In experimental procedure, the variable factor is usually the concentration (or pressure) while all the other conditions are held constant. A graphical representation of the data obtained is an isotherm in which the amount adsorbed per unit weight of adsorbent is plotted against the equilibrium concentration or pressure at constant temperature.

Since the extent and manner of adsorption is dependent on the nature of the adsorbent and adsorbate, a relatively large number of different shapes of these isotherms is possible. The simplest of these, and one commonly exhibited by charcoal, shows a very sharp rise starting with zero concentration or pressure and then a flattening out. Diagramatically it can be shown thus:
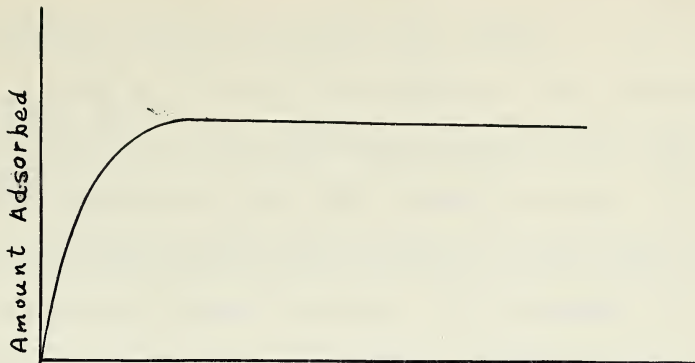
Equil. pressure or conc. of adsorbate.

Freundlich represented this type of graph mathematically as

$v = kp^{\frac{1}{n}}$ where v is the amount adsorbed, k is a constant, p is the equilibrium pressure or concentration and $n > 1$. The Freundlich isotherm offers quite a useful means of expressing and comparing adsorption results and is still widely used for that purpose. The defects inherent in it are 1) it only holds over narrow ranges, and 2) it is purely empirical having no theoretical basis. It is therefore of little use as a means of elucidating the mechanism of the adsorption process.

Langmuir, in his monomolecular layer theory, brought forth a more useful expression known as the Langmuir isotherm. Assuming an adsorbed layer only one molecule thick, he expressed the amount adsorbed as $V = \frac{Pbk}{1+Pk}$ where P is the equilibrium pressure or concentration and k and b are constants which hold for a given system. This algebraic expression may be resolved into

an equation for a straight line thus:

$\frac{P}{V} = \frac{1}{bk} + \frac{P}{b}$. P and V are obtained from experimental data.

The values of b and k may be obtained from the slope and slope-intercept of the P/V versus P graph. The value b has been shown to be the maximum volume that can be adsorbed by a given charcoal. The Langmuir isotherm applies well to the experimental data obtained in this work and has been used throughout.

Langmuir's isotherm works well in cases where Freundlich's isotherm fails, but is itself limited to monomolecular layer adsorption. Emmett, Brunauer and Teller, using a method which is a generalization of Langmuir's treatment of unimolecular adsorption, have developed an isotherm equation applicable to multi-molecula layers and capillary condensation as well (2).

A useful application involving adsorption is that of measuring surface areas of adsorbents. Two common methods in use for doing this involve adsorption from solution, and gas adsorption in an evacuated system. Of the two the former has been longer in use. The latter method has been given an impetus by the development of the Emmett apparatus with its easy manipulation and high accuracy (3).

Adsorption, as was previously mentioned, is a function of the nature of the adsorbate and adsorbent. In the case of a porous material, such as charcoal, one

would have to choose suitable adsorbates for determining its surface area. Garner, McKie and Knight (4) offer the following criteria in choosing these adsorbates:

(1) The longest molecular dimension should be smaller than the radius of the smallest capillary in the porous body.

(2) The molecule should be capable of packing easily in the surface and in such a manner that the lateral forces between the adsorbed molecules increase the stability of the film.

(3) The adsorbed molecules should be so oriented on the surface that the exposed groups of the molecules of the first layer exert weak subsiduary valency forces on the second layers, thus reducing the tendency to form multilayers.

The surface areas of many charcoals have been determined using acids and alcohols in adsorption from solution. Lemieux and Morrison (5) began investigating the adsorption of the low molecular weight mono-carboxylic acids and benzoic acid on a series of seven activated coconut charcoals. Miller and Morrison (6) extended this work to include the dicarboxylic and unsaturated dicarboxylic acids on the same series.

The work of Lemieux, Miller and Morrison indicated unimolecularity of adsorption of the fatty acids and has revealed much concerning the nature of the char-

coal pores. They have shown that the screening effect of the charcoal is an important factor in determining the amount of adsorption taking place. They have come to the conclusion that the acid molecules are oriented vertically on the charcoal surface. On the basis of this Miller has been able to calculate pore radii.

The object of the present work is to investigate the adsorption of the gaseous hydrocarbons on the same series with the use of the Emmett Apparatus. Although very little information concerning the adsorptive properties of these gases on such a series has been reported, some work has been done using methane, butane and nitrogen on a single charcoal. Miller(6) determined the amount of adsorption of nitrogen and butane by these charcoals. By comparison with the results of carboxylic acids which are oriented vertically, he considered that butane is oriented vertically also. This is contrary to the horizontal orientation postulated by Brunauer and Emmett, and others. He attributes the vertical orienta- tion of butane to adsorption by induced dipole formation, which considers adsorption to be a results of interaction between surface and adsorbed dipoles. Butane has a zero permanent dipole, but an induced dipole of 20.49 ml. along the long axis and 4.6 ml. along the short axis. Presumably vertical orientation would favor greater interaction and hence greater adsorption.

It is the object of this thesis to
investigate the hydrocarbon gases from methane to
butane in order to elucidate the nature of their
adsorption. In this way it may be possible to confirm
or deny the hypothesis of Miller and Morrison concerning
the orientation of butane on a charcoal surface.

EXPERIMENTAL

Experimental

The apparatus used for this work was one described by Emmett (3) and others. The diagram of the apparatus, with explanations and the principle of its operation, is given by Miller in his thesis (6).

The gases required for this work had to be extremely pure. This purity was obtained, with possibly the exception of propane. The propane and butane were obtained from the Ohio Chemical Company and were specified to be 99.9% and 99.9% pure respectively. However, propane behaved badly for charcoals 4, 5, 6 and 7, and a reason given for this behavior was the possible contamination of this gas by some foreign material in the tank or in the process of transfer to the storage bulb. Further investigation will have to be made to account for anomolous propane results.

Butane and propane were allowed to enter the evacuated storage bulbs after passing through purifying traps immersed in ice-water, and dry ice-acetone (-50°C) baths for the respective gases. This procedure could be improved; in the future it is suggested that these gases be liquified in a trap immersed in a dry ice-acetone bath at approximately -80°C. The non-condensable gases and lower molecular weight impurities would then be pumped off and the middle fraction allowed to evaporate

into the storage bulb to the desired pressure.

Purified tank nitrogen was used in this work. The purification involved passing the nitrogen through a $CrCl_2$ solution tower, then through anhydrous $CaCl_2$, P_2O_5 and soda-ash driers, and finally through a trap immersed in liquid air.

Pure methane was obtained by the low temperature fractionation (liquid air) of natural gas using a fractionating column described by Verschoyle (7).

Pure ethane was prepared by the hydrolysis of ethyl magnesium bromide. This gas was passed through fuming H_2SO_4, concentrated H_2SO_4, 20% KOH and pelleted KOH scrubbers and was finally fractionated using liquid air

Helium purchased from the Ohio Chemical Company was used. Prior to storage in the bulb it was passed through an activated charcoal trap cooled in a liquid air bath.

No quantitative analysis of the gases was made. In all cases they were assumed to be in a desirably pure state.

The dead space in the adsorption chamber was determined at $0^{\circ}C$ in the manner suggested by Brunauer and Emmett, and described by Miller (6). In this determination pure helium is used; being an inert gas it is adsorbed to a negligible extent. It was assumed that helium obeys the ideal gas laws. Hence the dead

space at any temperature (V_n) could be computed using
the equation $V_n = V \times \dfrac{273}{T_n}$ where V is the volume
of the dead space at N.T.P. and T_n is the temperature
of the adsorption chamber during a run.

The experimental work is based on a principle
suggested by Emmett and Brunauer, in which the adsorption
takes place at or near the boiling point of the gas.
However, to eliminate the possibility of capillary conden-
sation and to make more reproducible results possible,
use of a temperature several degrees above the boiling
point was found to be more satisfactory. The temperatures
used during the runs and the boiling points of the gases
are as follows:

Gas	B.P.	Temp. of bath	Nature of bath
N_2	$-195.8^{\circ}C$	$-190^{\circ}C$	liquid air
CH_4	$-161.5^{\circ}C$	$-145^{\circ}C$	heating coil surroun-ding the adsorption chamber and immersed in liquid air.
C_2H_6	$-88.3^{\circ}C$	$-80^{\circ}C$	dry-ice and acetone
C_3H_8	$-42.2^{\circ}C$	$-39^{\circ}C$	dry-ice and acetone
$n-C_4H_{10}$	$-.6$ to $-.3^{\circ}C$	$0^{\circ}C$	ice water

None of the gases used, apart from helium,
obeys the ideal gas laws so that it was necessary to
make corrections for this deviation from ideality. The
corrections for nitrogen, methane and n-butane were those
suggested by Brunauer and Emmett (8). No values for

propane and ethane could be obtained and no expérimental
data was available for computing this deviation. The
corrections made for these two gases were estimated on
the basis of their physical properties as compared with
those of similar gases. Only the "dead space" volumes
were corrected for the gas imperfections, and the new
volume V_b was expressed as $V_n \times \dfrac{100\% + h\%}{100\%}$ where h is
the deviation expressed as a percentage. h for the
various gases is as follows:

N_2	4.1%	@	$83^{\circ}K$
CH_4	5.9%	@	$145^{\circ}K$
C_2H_6	7.0%	@	$193^{\circ}K$
C_3H_8	8.3%	@	$234^{\circ}K$
$n-C_4H_{10}$	10.8%	@	$273^{\circ}K$

There is some doubt as to whether the correction is
important in this work; the necessity for it will be
determined by further investigation.

The same series of coconut charcoal (charge 35)
was used in this work as was used by Lemieux and Morrison,
and Miller and Morrison. This series is made up of
seven charcoals of different degrees of activation all
derived from the same original unactivated batch. The
data supplied with these charcoals are given in Miller's
thesis (6).

The amount of adsorption of each of the gases
on charcoals one to seven was determined employing the

method described by Miller (6). In calculating the amounts of adsorption of these gases, all volumes were referred to S.T.P. The amount of adsorption (V_a) was determined from

$$V_a = V_B + V_D - V_b - V_d \text{ where}$$

V_B = gas volume in the burette before adsorption,

V_D = amount of residual gas in the dead space following previous adsorption,

V_b = amount of gas in the burette following adsorption

V_d = amount of gas in the adsorption bulb following adsorption.

The values of P/V_a were plotted against P in accordance with Langmuir's isotherm. Good plots were obtained for all the gases. Only one run on each charcoal with each gas was made except for propane on charcoals 1, 4, and 7. The graphs shown in Fig. 4 for propane on these charcoals represent the average of several runs made on each.

The slopes of the straight lines were used to find the maximum adsorption (V_m) of each gas by the charcoals.

RESULTS

Results

The adsorption isotherms for nitrogen, methane, ethane, propane and butane are shown in figures 1 to 5 respectively. These isotherms indicate that the Langmuir equation applies well to the experimental data obtained.

The maximum volumes of gases adsorbed (V_m) were obtained from the slopes of the graphs. For the purpose of interpretation the volumes were converted to the maximum number of millimoles of gas adsorbed (Table I). The results obtained by Miller (6) on the same series with butane and nitrogen are given to show the effect of sampling and to ascertain the reproducibility of results.
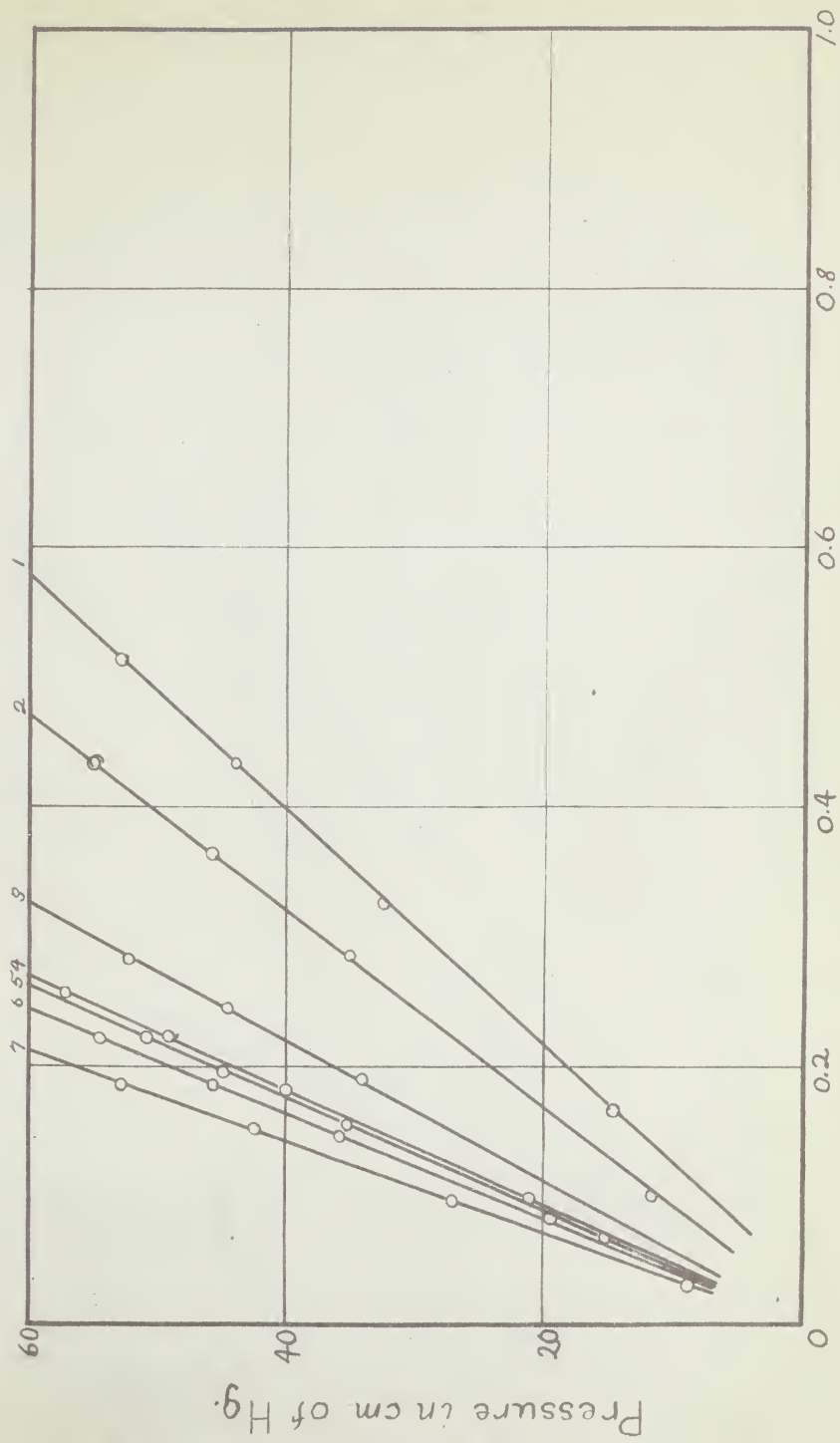
Table I

Maximum Adsorption of Gases in Millimoles per
Gram of Charcoal.

Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
Nitrogen	4.88	5.92	8.42	9.79	10.18	11.06	12.58
Methane	3.61	4.39	6.70	8.27	8.51	9.39	9.82
Ethane	3.00	3.40	4.84	5.66	6.15	6.54	7.65
Propane	1.92	2.31	3.78	5.07	5.18	5.63	6.19
n-Butane	1.29	1.77	2.68	3.28	3.68	4.00	4.62
Miller's Data							
N_2	4.80	6.38	7.59	10.00	11.10	11.80	14.60
n-Butane	0.95	2.03	2.38	3.68	3.93	4.14	4.64

P/V in cm. Hg per ml. Nitrogen Adsorbed per gm. Charcoal

FIG. 1 — Langmuir Plot for Nitrogen

Pressure in cm. of Hg.

P/v in cm. Hg. per ml. Methane Adsorbed per gm Charcoal
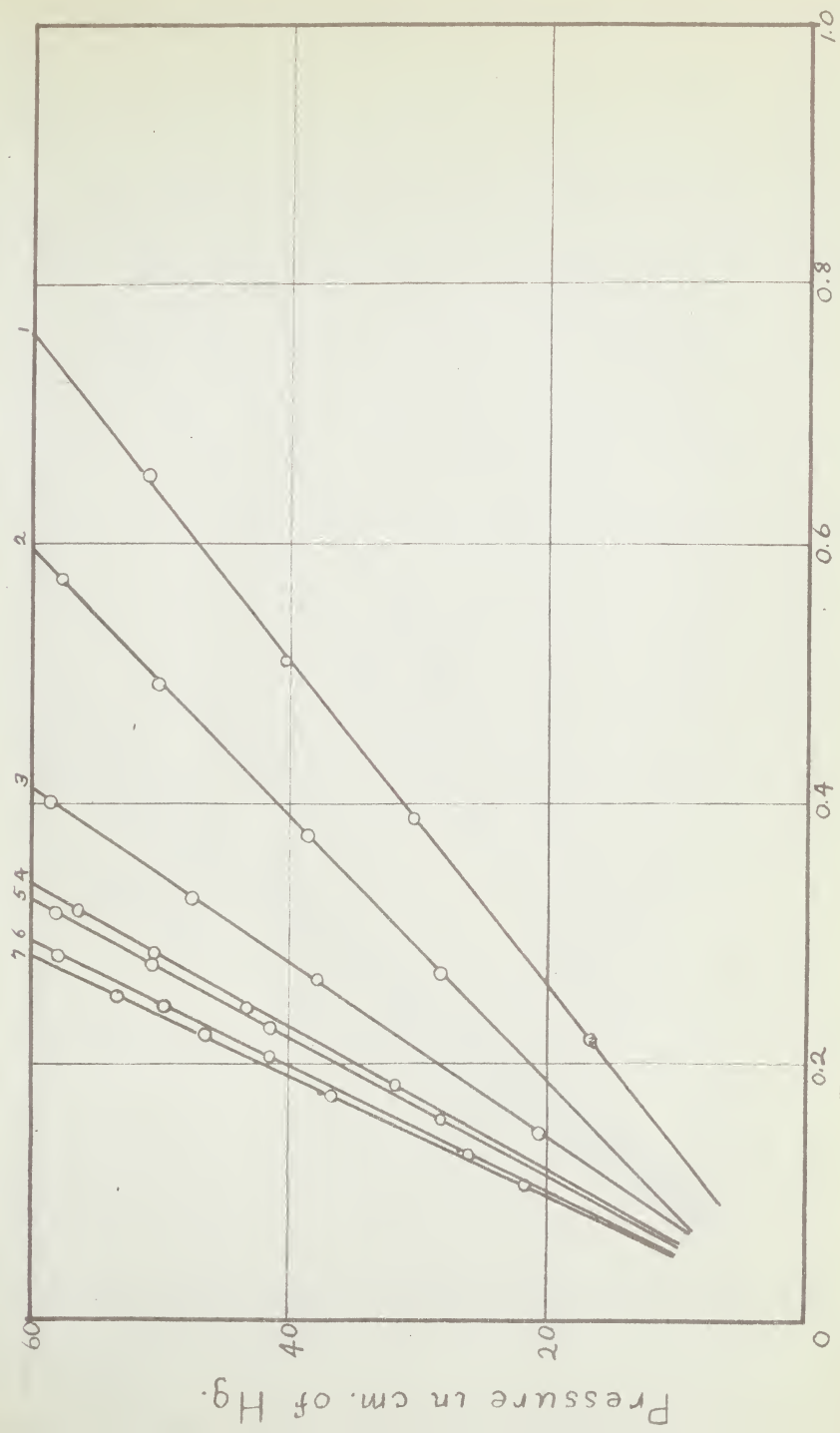
FIG. 2 — Langmuir Plot for Methane

P/v in cm Hg per ml. Ethane Adsorbed per gm Charcoal
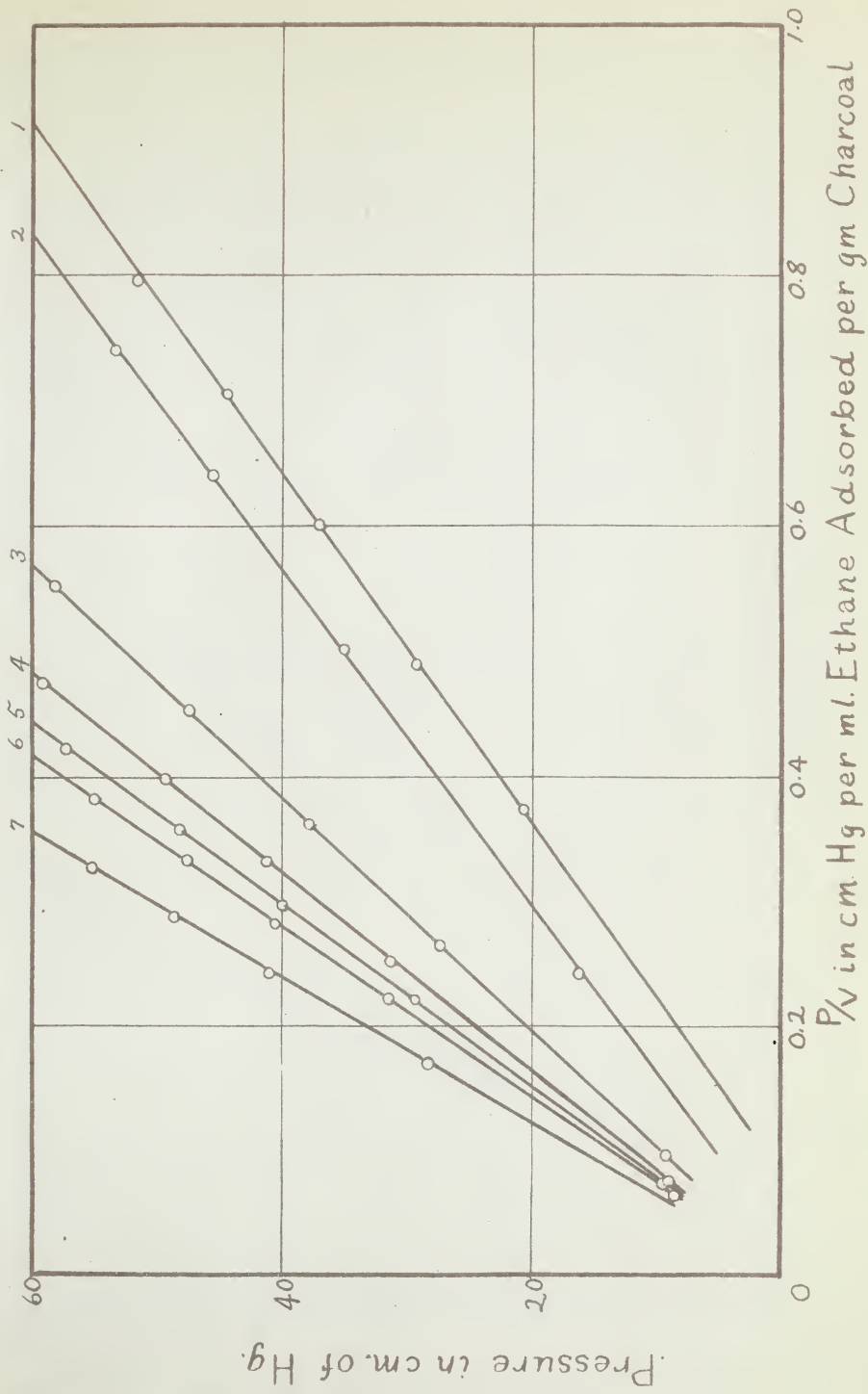
FIG.3 — Langmuir Plot for Ethane

Pressure in cm. of Hg.

P/v in cm Hg. per ml Propane Adsorbed per gm Charcoal
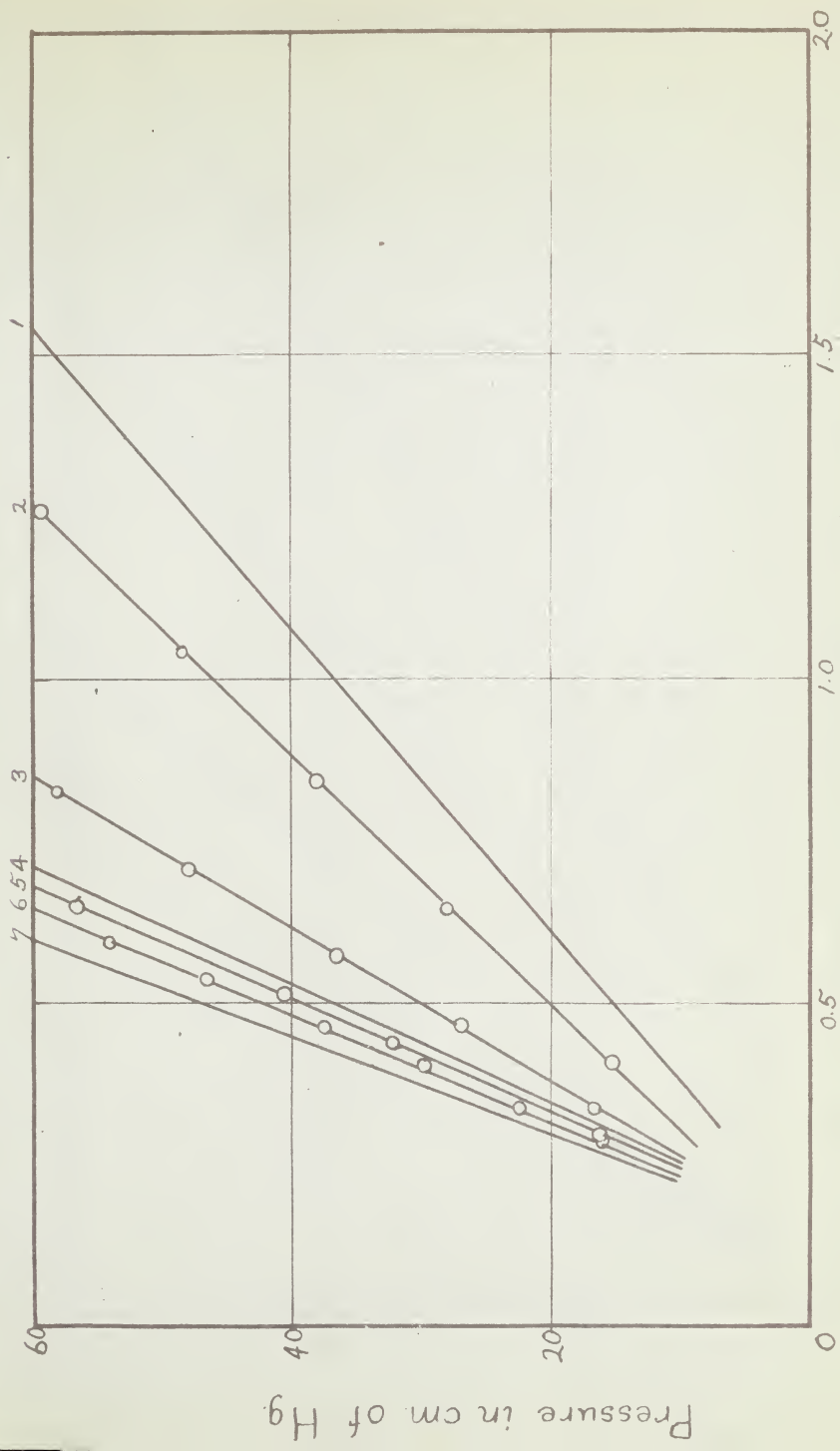
FIG.4 — Langmuir Plot for Propane

Pressure in cm of Hg
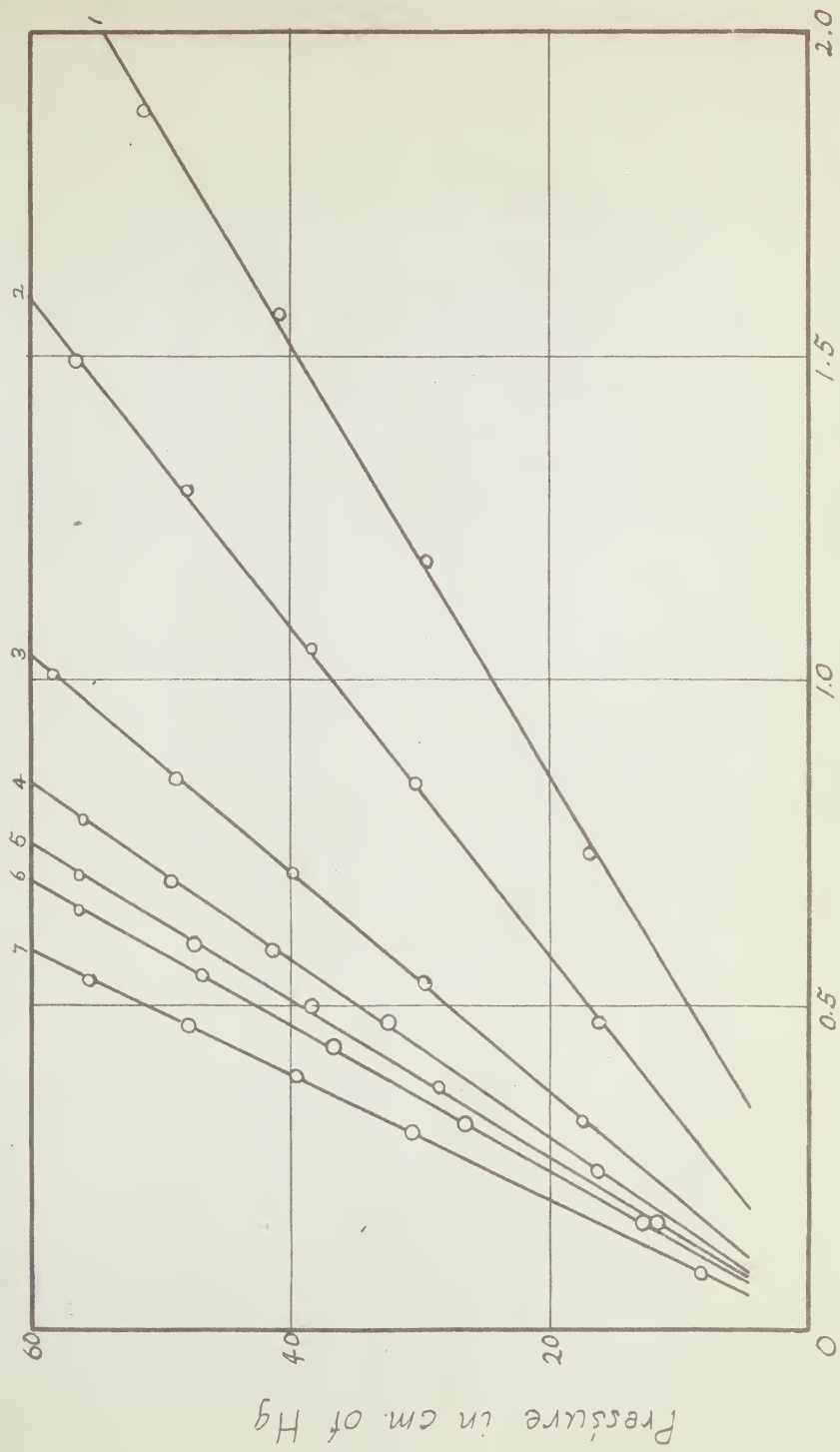
P/V in cm Hg per ml. Butane Adsorbed per gm Charcoal.

FIG.5 — Langmuir Plot for Butane

Pressure in cm of Hg

DISCUSSION OF RESULTS

Discussion of Results

It was stated previously that the surface area of an adsorbent could be determined from the maximum volume (V_m) adsorbed in a layer one molecule thick. The surface area in square metres per gram of adsorbent is given by $\frac{V_m N \sigma}{1000} \times 10^{-20}$ where V_m is the maximum adsorption in millimoles per gram, N is Avogadro's number and σ is the area covered by an adsorbate molecule and is expressed in square angstroms. In the following discussion this area will be referred to as the section area or effective adsorption area. It is not to be confused with the cross-sectional area of the molecule, that is, the area along the short axis.

Livingston (9) indicates that the surface area of a non-porous substance should be almost the same when determined by means of a variety of suitable adsorbates. This may not be necessarily true for porous materials such as charcoal because other factors enter into the mechanism of adsorption. Lemieux and Morrison (5) and Miller and Morrison (6) obtained charcoal surface areas which varied with the activation of the charcoal and the length of the fatty acid used. They suggested that the variation was due to the screening effect of the charcoal pores. The data presented in Table II on charcoal areas by gaseous adsorbates apparently substantiates their

results. That is, the areas obtained also vary with activation and molecular size. However, it will be shown that this variation in the surface areas may be due to quite a different mechanism.

Charcoal Surface Areas.

Some difficulty was encountered in obtaining the values for σ, the effective adsorption area of the gas molecules used. Values for some of them were reported in the literature but there was much discrepancy in these. Brunauer and Emmett used 13.8 A^{o2} for solid nitrogen packing and 16.2 or 17.0 A^{o2} for liquid packing (12). Gaudin and Bowdish have shown in their investigations the 13.8 value to be the more suitable area for nitrogen at liquid air temperature (10). Jura and Harkins (14) used 15.4A^{o2} consistently for nitrogen and justified the use of this value on the basis of sixty isotherms which they obtained. Brunauer and Emmett, assuming horizontal orientation, have calculated the section area for butane to be 32A^{o2}. Fineman, Guest and McIntosh, also assuming horizontal orientation, have used 48A^{o2} for butane in their work on a coconut charcoal series (11). Livingston (9) attributes these discrepancies in the section areas to the packing. For a given adsorbate this packing varies with temperature, surface pressure and the adsorbent. He states that a correct value for

the section area of a molecule would have to be obtained
from an inter-relation of areas obtained from adsorption,
X-ray, density and film-balance measurements.

The values for the effective adsorption areas
for Nitrogen, methane and butane used in this work are
those given by Brunauer and Emmett in one of their
papers (12). The section areas of propane and ethane
were computed from data given by Hendricks (13). All
these values are based on the assumption that the
molecules are oriented horizontally, either in solid or
liquid packing.

The surface areas of the charcoals investigated
in this work are given in Table II. The charcoal areas
for both liquid and solid packing were determined in the
case of nitrogen, methane and butane.

Set I gives the surface areas determined in the
present work. Set II gives the charcoal areas determined
by Miller with nitrogen on the same charcoal series as
was used for set I. Set III gives the surface area data
obtained by Fineman, Guest, and McIntosh on a similar

Footnotes to Table II:
(1)   (a) - the section area for solid packing
(2)   (b) - the section area for liquid packing
(3)   This value for σ is the one calculated by Miller
       (6) on the basis of vertical orientation of butane.

Table II

Charcoal Areas (in square metres per gram) for Gas Adsorbates on Charge 35.

Adsorbate	σ(A°2)	\ Charcoal Number /						
		1 / A	2 / B	3 / C	4 / D	5 / E	6 / F	7
I								
nitrogen	13.8(a)[1]	408	495	704	819	852	924	1052
	17.0(b)[2]	503	610	867	1008	1049	1138	1295
methane	15.0(a)	328	399	609	752	773	854	892
	18.1 (b)	396	481	735	907	933	1030	1077
ethane	20.0 (a)	264	404	587	686	744	793	927
propane	23.5(a)	274	329	538	722	738	802	875
n-butane	32.0(a)	250	343	520	636	714	776	896
	20.0 (3)	156	215	325	398	446	485	560
II								
nitrogen	13.8(a)	401	534	635	837	930	987	1220
III		A	B	C	D	E	F	
nitrogen	17 (b)	644	749	895	963	1070	1140	
n-butane	32.1 (b)	333	417	553	602	703	737	
	48.0 (b)	500	625	829	903	1050	1100	

coconut charcoal series (11). The last two sets are
included for comparison. There is fairly good agreement
among the three sets. A comparison of sets I and II
indicates the effect of sampling. When comparing the
data in set I and II, one must remember that the histories
of the two charcoal series differ.

Surface Orientation

The maximum number of millimoles of nitrogen,
methane, ethane, propane and butane adsorbed by each
charcoal were plotted against the number of millimoles
of butane adsorbed (Fig. 6). The butane versus butane
graph is a straight line at 45° with the horizontal axis.
It was believed that if these plots gave lines which
eventually met, or showed a tendency to meet each other
towards the charcoals of high activity, then this would
be an indication of orientation of the same nature as
that encountered with the acids on charge 35 (5).
However, the graphs obtained showed a contrary behavior
as figure 6 indicates. The maximum numbers of millimoles
adsorbed by the charcoals increase both with increasing
activation and decreasing molecular size rather than
approach a common V_m with increasing activation as was
the case with the acids (compare values in Tables I and
IA). The fact that the number of millimoles adsorbed,
when plotted against butane, diverge with increasing
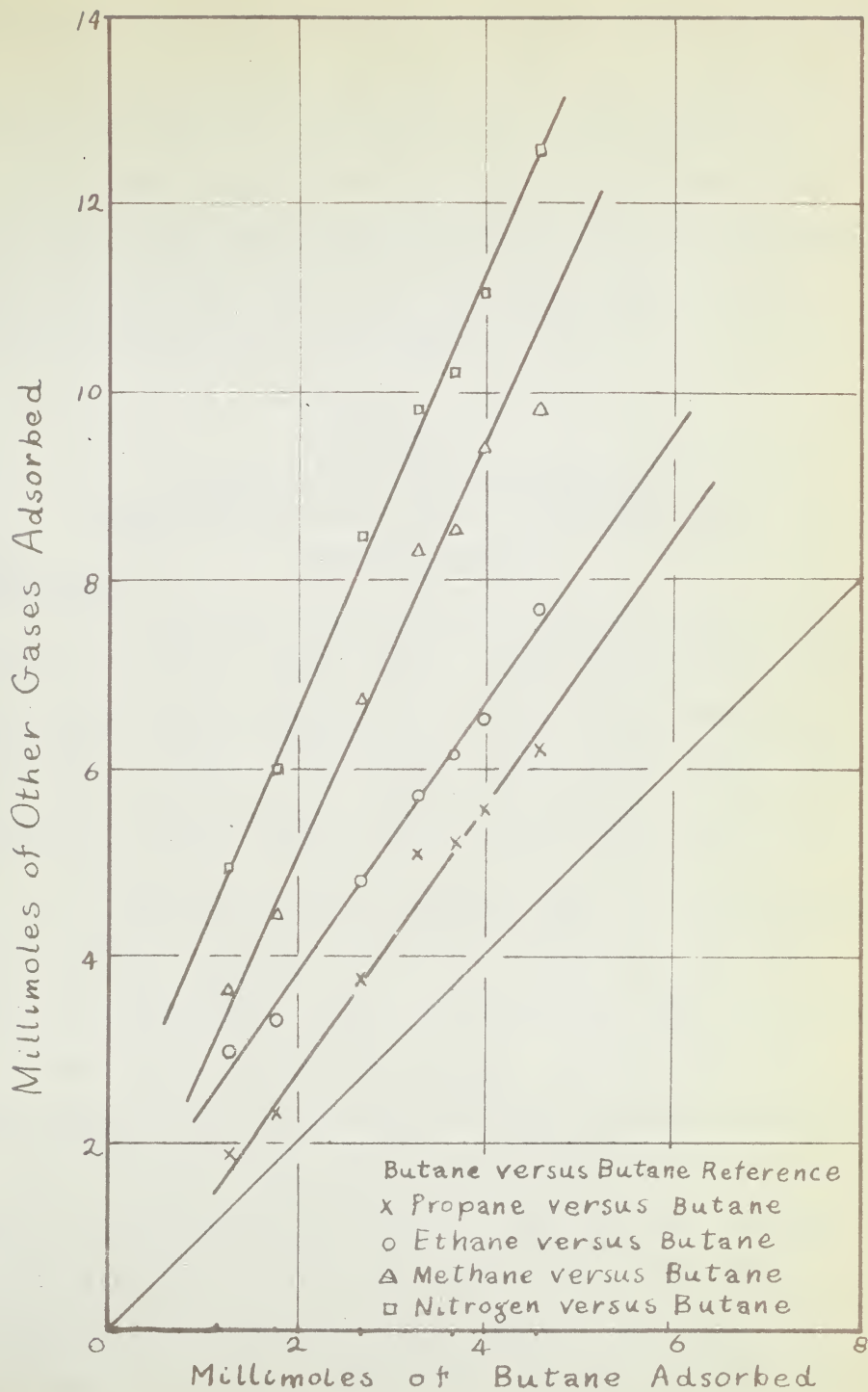activity instead of converge as do the straight-chained

FIG. 6 – Millimoles versus Millimoles Chart

aliphatic acids (5) indicates that the orientation of the
gas molecules differs from that of the acid molecules.
Whereas in vertical orientation the screening effect
and molecular length were the controlling factors, in
the case of the gaseous hydrocarbons there are indications
that the important factor is the area occupied by a
molecule horizontally oriented.

Table IA

Maximum Number of Millimoles of Acid Adsorbed per Gram of Charcoal. (5)

Acid Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
acetic	2.15	2.55	2.85	3.22	3.25	3.70	4.00
propionic	1.63	2.04	2.47	2.91	2.93	3.46	3.75
butyric	1.24	1.66	2.06	2.63	2.74	3.43	3.84
valeric	0.88	1.31	1.75	2.40	2.41	3.18	3.66

At this point it might be well to differentiate
between horizontal and vertical orientation. Lemieux,
Miller and Morrison (5, 6) have indicated that the pores
in these charcoals are cone-shaped. They assume these
cone-shaped pores on the basis of the vertical orientation
of the acid molecules. In vertical orientation the long
axis of the molecule is normal to the charcoal surface.
The limitations in this type of adsorption are the
screening effect and the chain length. From this
argument it is easy to understand why the maximum

volumes of acid adsorbed approach each other with the
increasing activity of the charcoals. (Table IA). At
lower activations the number of millimoles of the larger
molecules adsorbed are reduced by screening but at higher
activations approach each other because of the reduced
screening effect. This would be expected if the
orientation were in such a way that the area occupied by
each molecule were the same.

In horizontal orientation it will be assumed
that the same areas are available to the various gases.
Then the amount adsorbed would depend on the effective
adsorption area of the molecule (assuming a unimolecular
layer). The maximum volume adsorbed (V_m) is inversely
proportional to this area. One would expect such a
relation to give divergence in a millimoles adsorbed
versus millimoles adsorbed plot.

Diagram of Vertical and Horizontal Orientation

Acid adsorption   Proposed gas adsorption
(vertical)   (horizontal)

Let us assume that the orientation is
horizontal. Such an assumption can be substantiated
with evidence from the literature. Brunauer and
Emmett (12) have indicated that butane is oriented with

the long axis parallel to the solid surface of an iron
catalyst. Livingston in his work with n-heptane on
smooth surfaces (including graphite) found that the
section area of heptane corresponds to horizontal rather
than vertical orientation.

In discussing horizontal orientation the writer
usually implies equal, or approximately equal surface
areas available to all adsorbates providing their
molecular thickness is of little or no importance. The
fairly constant ratios in Table III (given later) seem to
indicate that the same areas are available to all the
gases. Hence the area of a given charcoal should be
almost the same regardless of which of the gases is used.
The limitation is the accuracy of the values for the
section areas of the gas molecules used. According to
Livingston (9) these areas would be expected to vary for
different adsorbents so that the values used in this work
in computing the charcoal surface areas may not
necessarily be correct.

However, any error in the effective adsorption
area of any one molecule would be carried through for the
seven charcoals. With this in mind it may be possible to
compare the surface areas of the charcoals in another
manner. A comparison was made in figures 7 and 8 where
the surface areas of the seven charcoals as determined
with nitrogen, methane, ethane and propane were plotted
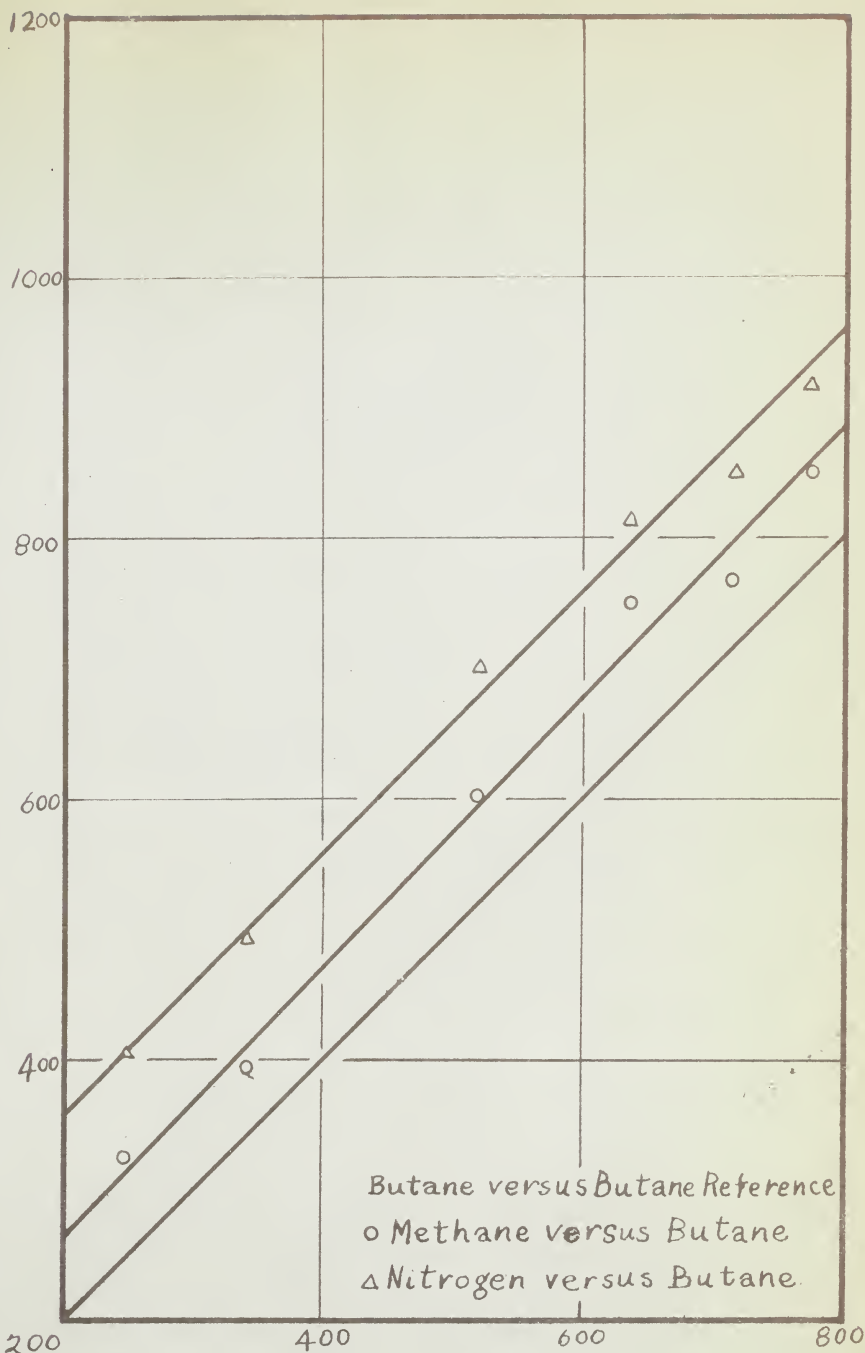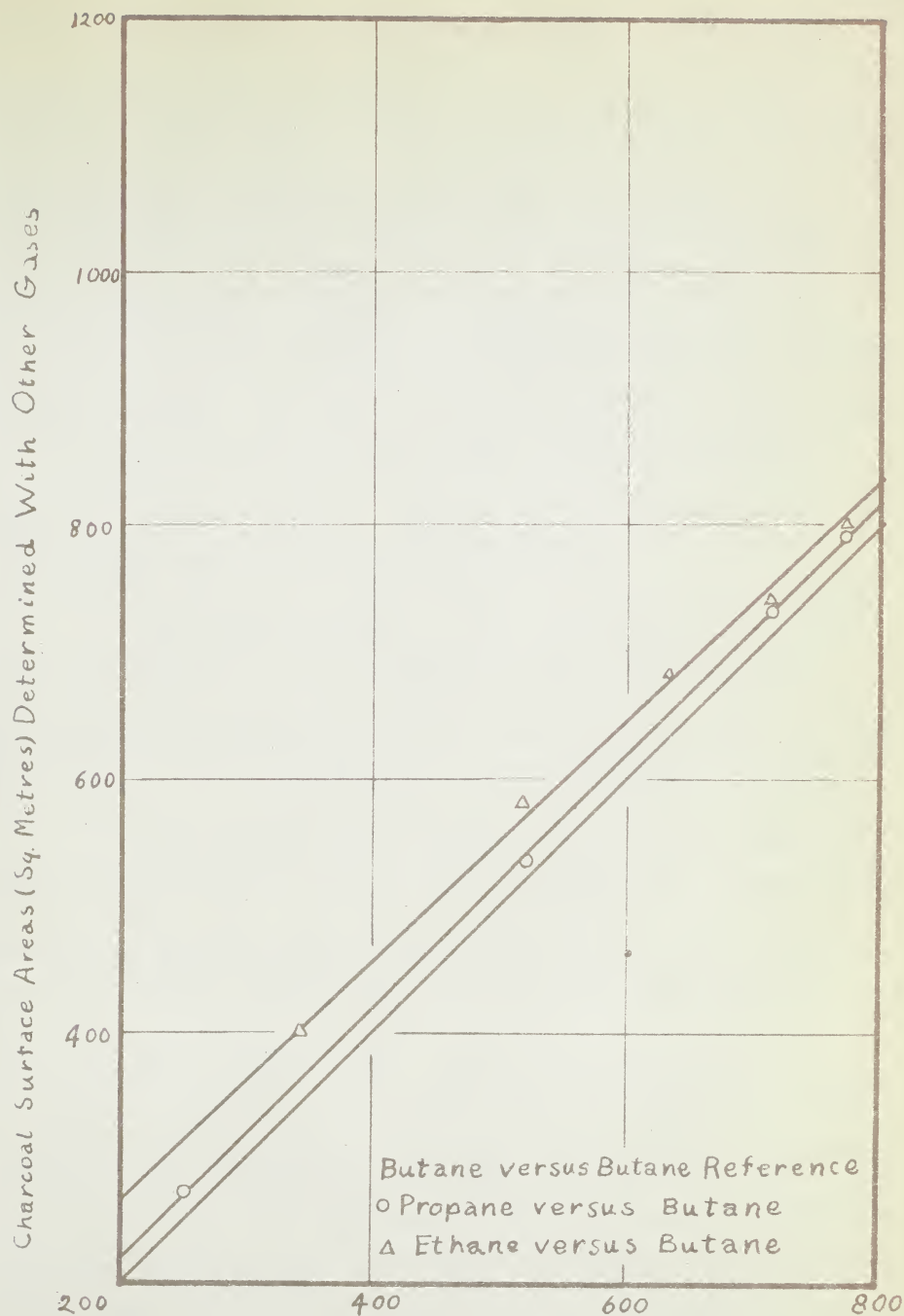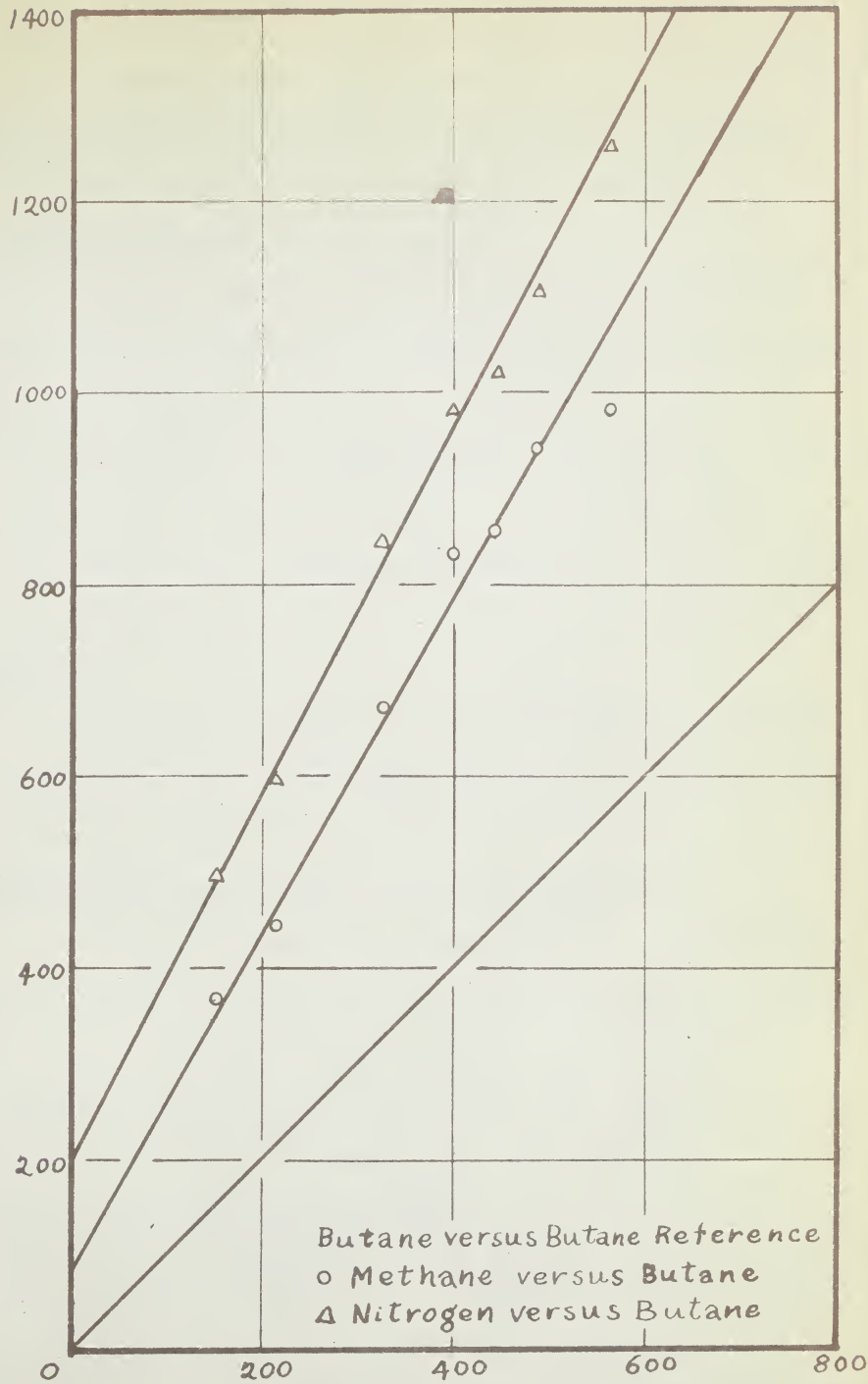
FIG. 7— Surface Areas versus Surface Areas Chart

FIG.8 – Surface Areas versus Surface Areas Chart

against the surface areas given by butane. The areas
plotted were those determined on the basis of solid
packing. On the basis of the assumptions made (that the
molecules are horizontally oriented, and that
approximately the same areas are available to all the
gases), the graphs obtained in such a plot should be
parallel or nearly parallel to the reference line (butane
versus butane). It can be seen from figures 7 and 8 that
the lines for the gases are nearly parallel to the
standard line of butane. This seems to indicate that the
assumptions made initially are correct.

The displacement of the approximately parallel
lines in figures 7 and 8 indicates the possibility of
finding more accurate values for the section areas of the
molecules. This possibility will be discussed later.

It is generally accepted that the nitrogen and
methane molecules are spherical or nearly so. Hence they
should not behave differently whether the other hydro-
carbon gases are vertically or horizontally oriented
when adsorbed by charcoal. Using this characteristic
of these two gases it would probably be possible to con-
firm or disprove Miller's vertical orientation hypothesis
for butane (6). The surface areas of the seven charcoals
obtained from nitrogen and methane adsorption were plotted
against the surface areas computed on the basis of Miller's
cross-sectional area of $20A^{o2}$ for butane (Fig. 9).

FIG. 9 — Surface Areas versus Surface Areas Chart

The lines are not at all parallel to the butane versus butane reference line. This behavior is to be expected from the argument presented in the previous paragraph and further confirms the horizontal orientation hypothesis proposed in this thesis.

Miller based his hypothesis on (1) the approximately equal adsorption of butane and the low-molecular-weight monocarboxylic acids by charcoals 6 and 7, and, (2) for these activated charcoals butane would be expected to have access to the same area as the acids. The present work with the gaseous hydrocarbon series does not justify Miller's deduction of vertical orientation for butane.

On the basis of the above arguments it may be concluded that the hydrocarbon homologs are horizontally oriented when adsorbed by a charcoal surface.

Effective   Adsorption   Areas of Molecules

It was previously suggested that the displacement of the lines from the butane versus butane reference line in figures 7 and 8 indicates the possibility of determining more accurate values for the effective adsorption areas of the molecules. The ratios,

millimoles of nitrogen adsorbed
millimoles of hydrocarbon adsorbed, were determined for all the hydrocarbon gases for the whole charcoal series. These ratios are given in Table III. Similar ratios could be worked out using any of the other gases as the

Table III

Ratios, $\dfrac{\text{Millimoles of Nitrogen Adsorbed}}{\text{Millimoles of Hydrocarbon Adsorbed}}$, for

Gas Adsorbates on Charge 35

| | Charcoal number | | | | | | | |
	1	2	3	4	5	6	7	Average
$\dfrac{\text{Nitrogen}}{\text{Methane}}$	1.35	1.35	1.26	1.18	1.20	1.18	1.28	1.26 ± .06
$\dfrac{\text{Nitrogen}}{\text{Ethane}}$	1.63	1.78	1.74	1.73	1.66	1.69	1.64	1.69 ± .05
$\dfrac{\text{Nitrogen}}{\text{Propane}}$	2.54	2.62	2.23	1.93	1.97	1.96	2.03	2.02 ± .08
$\dfrac{\text{Nitrogen}}{\text{n-Butane}}$	3.78	3.35	3.14	2.99	2.77	2.76	2.72	2.75 ± .02

reference gas but the one set will be sufficient here.

It is interesting to note that the ratios for methane and ethane are fairly constant throughout the charcoal series. For propane and butane the ratio decreases with increasing charcoal activity until it reaches a fairly constant value starting with charcoal 4 for propane and charcoal 5 for butane. However, this does not account for the displacement from the reference lines of the surface area versus surface area lines in figures 7 and 8. This displacement may be partly accounted for if a comparison of tables III and IV is made.

Table IV gives the ratios of the effective adsorption areas of the gases. Since $V_m \propto \frac{1}{\sigma}$ for any gas adsorbate, then the V_m ratios correspond to the inverse σ ratios.

Table IV

Ratios, $\dfrac{\text{Hydrocarbon Section Area}}{\text{Nitrogen Section Area}}$, for Gas Adsorbates

Gas	Section Area	Hydrocarbon section area / Nitrogen section area
nitrogen	13.8	
methane	15.0	1.09
ethane	20.0	1.45
propane	23.5	1.70
n-butane	32.0	2.32

It can be seen that the average V_m ratios in table III are in all cases much larger than the

corresponding ratios for σ in table IV. The V_m values
are experimentally obtained and are in error by an amount
which is determined by the experimental procedure used.
The σ values are only estimated approximately and so are
more liable to error. The effect of a low value for σ
can be illustrated thus:

Let us determine the surface area of a charcoal by
means of a gas A.

This surface area $\propto V_m \sigma = k V_m \sigma$

Let σ be the true section area of the gas A molecule,
therefore, will give the true surface area of the charcoal.

Hence for any $\sigma_1 < \sigma$, the surface area determined
would be less than the true surface area.

This is presumably what has happened in the
present work. The σ values for all the gases used are
lower than the true values. Hence all the charcoal
surface areas given in Table II are too low.

If the ratio between the σ values used in this
work is the same as the ratio between the true values,
then one would expect the surface area of a given char-
coal to be approximately the same regardless of the gas
used for determining it. From Table II it is apparent
that the ratio of the σ values used in this work is not
the same as the ratio of the true values for the section
areas of the gases. The surface areas given in table II

are in error by an amount which is proportional to the
variations in the two ratios mentioned. To illustrate
a little more fully take the case of butane and propane.
Presumably the ratio of their section areas used in this
work is closest to the true ratio of their section areas
because from figure 8 one can see that the propane versus
butane line is least displaced from the reference line
(butane versus butane). There is a greater discrepancy
between the present σ ratios from the true ratios for
butane and the other gases, hence a greater displacement
of their lines from the reference one.

The above argument indicates that it should be
possible to calculate the effective adsorption areas of
the gas molecules from the adsorption data. Livingston
substantiates this suggestion by saying that it is possible
to determine the section areas of adsorbates adsorbed by
non-porous solids. To be able to do so in the case of
porous materials the molecules would have to be adsorbed
horizontally so that the screening effect would be at a
minimum. That is, each adsorbate would have to have
access to approximately the same surface area. In this
work this criterion is satisfied, particularly for the
more activated charcoals. In order to be able to
calculate the effective adsorption areas of the gas
molecules, a particular gas must be taken as a standard.
Nitrogen is perhaps the simplest molecule and its section

area is most accurately known. Using either of the nitrogen values, 13.8 A^{o2} (solid packing) or 17.0A^{o2} (liquid packing), the effective adsorption areas of the other gas molecules may be obtained from the relation

$$\frac{V_m \text{ for nitrogen}}{V_m \text{ for hydrocarbon}} \times 13.8 \text{ (or 17.0).}$$ The areas which were thus obtained are given in Table V. (column a is N_2 solid packing, column b is N_2 liquid packing).

The average of all the areas of methane and ethane was taken because they are fairly constant for the whole charcoal series. For propane only the values for the last five charcoals and for butane the last three charcoals are averaged.

Livingston indicates that the effective adsorption area varies with the adsorbent. Hence it is safe to state that the average values for the effective adsorption areas determined from the adsorption data are probably more accurate than those used in determining the surface areas given in Table II. However, the section areas determined from the adsorption data are not entirely justified either. The reason why they are not fully justified will be discussed later.

It is interesting to note that the 46.7 A^{o2} value for liquid packing of butane is in good agreement with the 48 A^{o2} value used by Fineman, Guest and McIntosh for butane (11).
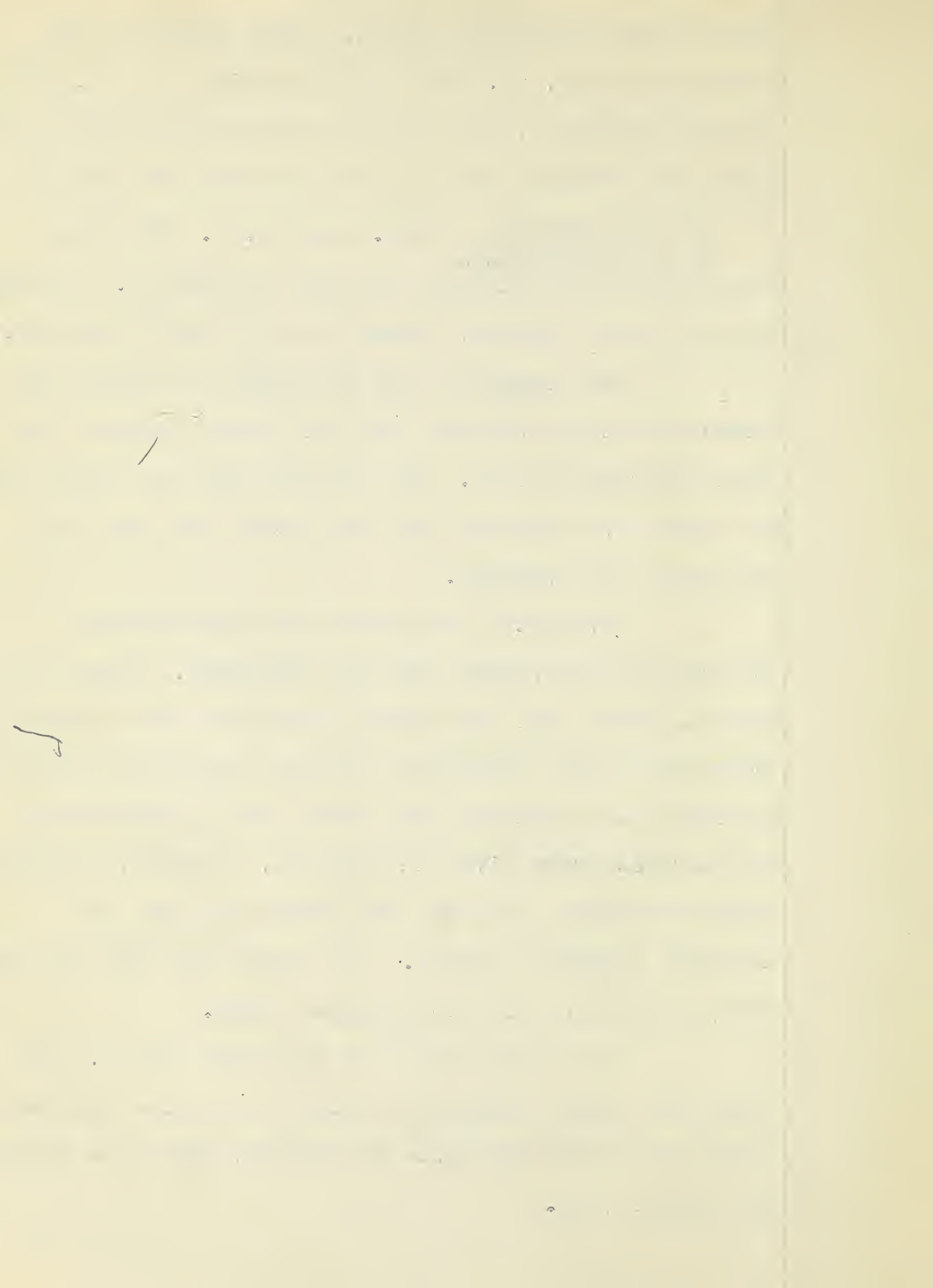
Table V

The Effective Adsorption Areas (in Å²) of the
Gaseous Hydrocarbons from Adsorption Data.

Adsorbate	Charcoal number											
	1		2		3		4		5		6	
	a	b	a	b	a	b	a	b	a	b	a	b
methane	18.6	22.9	18.6	22.9	17.4	21.4	16.3	20.1	16.6	20.4	16.3	20.1
ethane	22.5	27.7	24.6	30.3	24.0	29.6	23.9	29.4	22.9	28.2	23.3	28.7
propane	35.1	43.2	36.2	44.5	30.8	37.9	26.6	32.8	27.2	33.5	27.1	33.3
n-butane	52.2	64.2	46.5	56.9	43.3	53.4	41.3	49.1	38.2	47.1	38.1	46.9

	Average			
	a	b	a	b
methane	17.7	21.8	17.4	21.4
ethane	22.6	27.9	23.4	28.7
propane	28.0	34.5	27.9	34.2
n-butane	37.5	46.2	37.9	46.7

The average values for the effective adsorption area in Table V have been used to recalculate the surface areas of the seven charcoals. These are given in Table VI. The five values for the surface area of any one charcoal are in good agreement with one another except in the case of the less activated charcoals for which propane and butane show an anomalous behavior.

Table VI

Charcoal Areas (in square metres per gram)
Calculated on the Basis of the New Effective Adsorption Areas

Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
nitrogen	408	495	704	819	852	924	1052
methane	372	452	690	852	877	967	1011
ethane	418	473	674	789	857	911	1066
propane	326	392	642	861	829	956	1050
n-butane	297	407	617	755	847	921	1063
Average	399	473	689	820	852	936	1048

More accurate values for the surface areas of the charcoals are obtained by averaging the areas of any one charcoal (Table VI). Only the values given by the first three gases were used in finding the average surface areas of charcoals 1, 2 and 3. The average surface areas of charcoals 4, 5, 6 and 7 were obtained by

averaging the values given by the five gases.

Screening Effect

The discussion till now has been based on the assumption that approximately the same surface areas are available to all the gases. This is substantiated to some extent by Table III. However, this table also indicates that for the less activated charcoals butane and propane do not behave the same as the other gases. It is possible to explain this anomolous behavoir on the basis of the screening effect of the charcoal pores.

The gas molecules have a thickness which may be quite important in determining their penetrability into the finer pores. The diameter of the nitrogen molecule is from 3.0 to 3.5 A^o. Methane and ethane each have a thickness of about 4 A^o. Butane and propane are thicker. In these two gases the carbons are not situated in a straight line but in planes intersecting each other at $109^o 30'$. The carbons are situated at the apices of consecutive intersecting planes. This accounts for their greater thickness which is approximately 4.5 to 5.0 A^o. The greater thickness of the butane and propane molecules would indicate that they may be screened by the finer pores in the lower activated charcoals. However, as the activity of the charcoal increases, the statistical distribution of pores sizes shifts in the direction of the larger pores. Consequently

these thicker molecules gain access to approximately the same areas, as is indicated in tables III and V.

In the previous section the effective adsorption areas of the hydrocarbon molecules were determined from the adsorption data on the basis of the area occupied by a nitrogen molecule. Also cone-shaped pores were assumed as suggested by Lemieux and Morrison (5). The fact that the thickness of the hydrocarbon molecules varies from that of nitrogen would suggest that the hydrocarbon gases do not have access to quite the same areas. This is probably true because the nitrogen molecule can penetrate further into the cone than can any of the others. Similarly methane and ethane can penetrate further than propane and butane. This would indicate that the calculated effective adsorption areas in table V are somewhat in error. Actually this should be a very slight error because the surfaces at the apices of the cones are probably only a small fraction of the total surface. Furthermore it would be very difficult to determine this small fraction of the total surface area to which only the smaller molecules have access. Hence it is impossible at this point to correct the value given for the section areas in Table V.

In conclusion it must be noted that all calculations of charcoal surface areas and effective adsorption areas of the gases are based on the area occupied by nitrogen at the gas - charcoal interface. They can therefore, be only as accurate as the values $(13.8A^{o2}$ or $17.0A^{o2})$ used for nitrogen.

CONCLUSION

Summary

The adsorption of nitrogen, methane, ethane, propane and butane by a series of charcoals (with increasing activity) was measured using an Emmett adsorption apparatus.

The surface areas of the charcoals in this series were determined using the values given by Brunauer and Emmett for the effective adsorption areas of nitrogen, methane and butane and the values for the effective adsorption areas of propane and ethane calculated on the basis of data given by Hendricks.

By comparing the results of Lemieux, Miller and Morrison with those obtained in this work it was possible to show that the hydrocarbon molecules are oriented horizontally on a charcoal surface.

The present work does not confirm Miller's hypothesis of vertical orientation of butane.

The effective adsorption areas of the hydro-carbon molecules were calculated from the adsorption data on the basis of (1) the substantiated assumption that approximately equal areas were available to all the gases, and (2) the assumption that the values of 13.8 or 17 A^{o2} for the section area of nitrogen are quite accurate.

The surface areas of the charcoals in this series were recalculated using these new effective

adsorption areas of the gases. There was good
agreement between all the gases for the surface area
of any one charcoal.

There are indications of some screening effect
for all the gases but it is most evident for propane
and butane. The screening effect of the gas molecules
is determined by their thickness rather than by their
chain lengths.

Suggestions for Future Work

1.   Only the straight-chained hydrocarbon gases
were studied in this work. It should be possible to
determine the adsorption of isobutane by this charcoal
series with the Emmett adsorption apparatus. The higher
homologs such as the liquid pentane, hexane and heptane
isomers could be studied with the use of a McBain and
Bakr sorption balance.

2.   Livingston suggests that the effective
adsorption area of an adsorbate molecule may be obtained
by working with it on a non-porous adsorbent in conjunc-
tion with an adsorbate whose area is quite accurately
known. Hence it should be possible to determine the
section areas of the gaseous hydrocarbons using a non-
porous adsorbent. The values thus obtained could be
compared with the section areas given in Table V .
This would bear out the importance of the screening
effect in the adsorption of these gases by charcoal.
Furthermore such investigations would give further proof
to the exact nature of the orientation of these gas
molecules.

3.   The heats of adsorption of the hydrocarbon
gases may be determined by working at two different
temperatures and using the Clausius-Clapeyron equation.

4.   In this work the time allowed for adsorption
equilibrium to be reached was the same for each gas.
This procedure is probably not fully justified since
the time for equilibrium to be reached may not be the
same for each gas. Because the sizes of the molecules
differ, the rate of diffusion of the molecules into the
pores may have some importance in determing the amount
of a gas being adsorbed. It is suggested that experi-
mental proof be obtained whether the rate of adsorption
is the same for all gases and, if it is not, that the
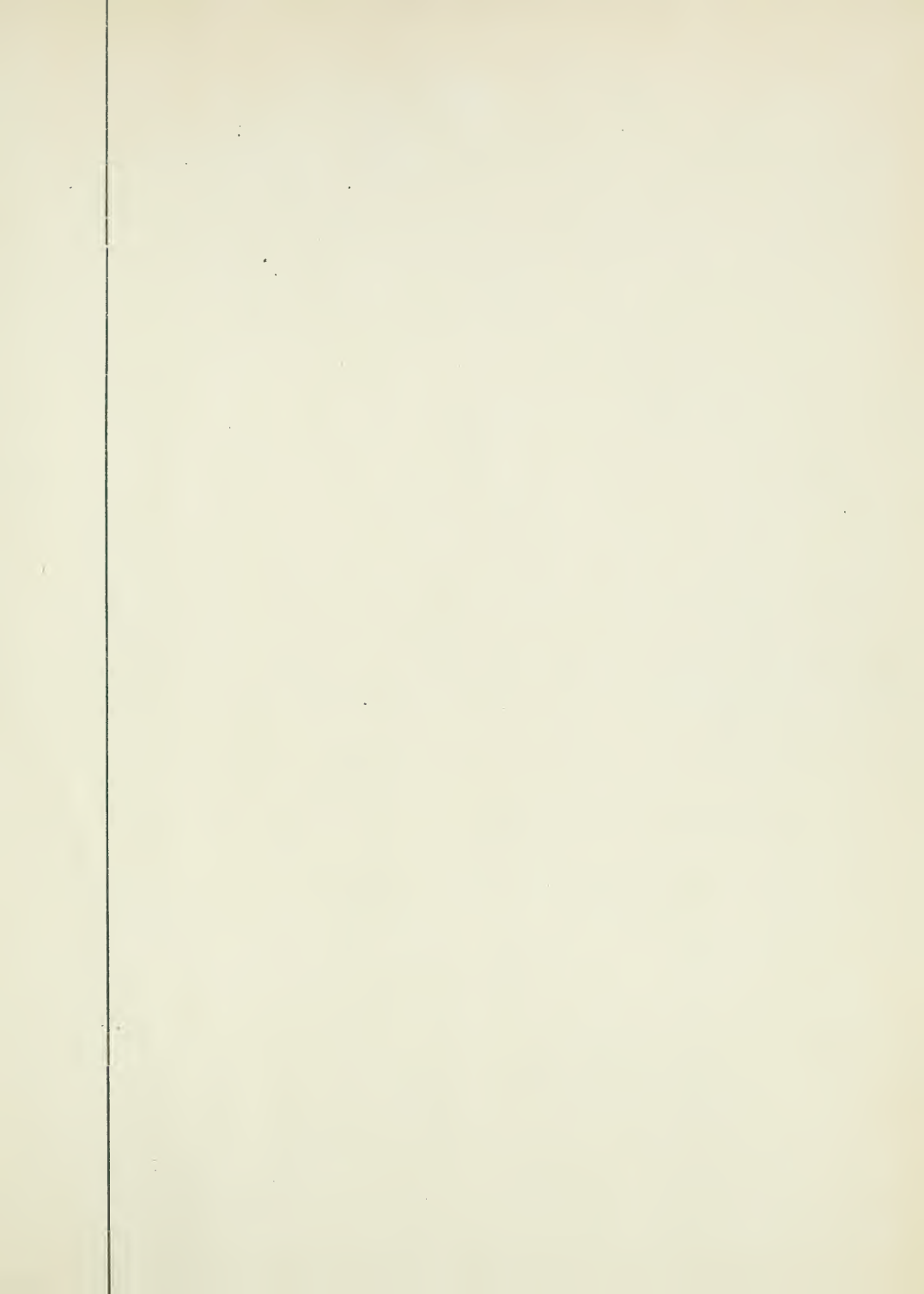rate of adsorption be determined for each individual gas.

5.   There is much confusion in the literature not
only as to what the effective adsorption area should be
but also whether solid or liquid packing takes place in
adsorption at the boiling points of the gases. It is
suggested that it may be possible to determine the
exact nature of the packing.

6.   In this work very little consideration has been
given to the activity of the respective charcoals. The
rate of activation, starting with the crude charcoal,
could probably be correlated with the amount of
adsorption taking place, hence elucidating the nature and
rate of pore formation. Activation of a given weight
of crude charcoal results in a loss in weight between
the initial and the higher activated one. This loss in

weight should be equivalent to the pore-volume. An
inter-relation of pore-volume and charcoal surface area
should give the magnitude of pore radii. Unfortunately
very little activation data is available on this
charcoal series to make such a study possible.

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